

Arrested state of clay-water suspensions: gel or glass?

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The aging of a charged colloidal system has been studied by Small Angle X-rays Scattering, in the exchanged momentum range $Q=0.03 \div 5 \text{ nm}^{-1}$, and by Dynamic Light Scattering, at different clay concentrations ($C_w=0.6 \% \div 2.8 \%$). The static structure factor, $S(Q)$, has been determined as a function of both aging time and concentration. This is the first direct experimental evidence of the existence and evolution with aging time of two different arrested states in a single system simply obtained only by changing its volume fraction: an inhomogeneous state is reached at low concentrations, while a homogenous one is found at high concentrations.

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In recent years, dynamical arrest in colloidal, and more generally in soft matter systems, has gained increasing attention [1]. Specifically, much effort has been devoted to clarify the dynamical behavior at large packing fraction, where the dynamical arrest is commonly identified as a kind of "glass transition". In colloids where both short range repulsion and attraction are present, a rich phenomenology is found: a re-entrant liquid-glass line, two kinds of glasses (named "attractive" and "repulsive") and a glass-glass transition line have been predicted and experimentally observed [2]. Very recently an increasing attention has also been devoted to the arrest at much smaller densities, in the usually called "gel region" of the phase diagram [1]. Experimental and simulation [3] studies have proven that, for hard-core plus spherically symmetric pair-wise attractive potentials, arrest at low density occurs only through an interrupted phase separation. More complex attraction is necessary to produce *gelation in equilibrium* which takes place when the gel state is reached continuously from an ergodic phase. This occurs when a long-range repulsion, induced for example by residual charges on the colloidal particles, is added to the short range depletion attraction [4]. Very recently a suppression of the phase separation has also been achieved by using an anisotropic interaction potential [5]. In this scenario lowering the "coordination number", i.e. the number of nearest neighbors allowed by the interaction potential, pushes the spinodal line to lower and lower packing fraction opening up the possibility to reach very low temperature (and hence states with extremely long bond lifetimes) without encountering phase separation. This permits the formation of an *equilibrium bonding gel*, i.e. a spanning network of long-living "physical" bonds at very low colloids concentrations [1].

The study of different arrested states in colloidal systems is therefore of crucial importance. In fact gels and glasses have often been viewed in an unifying framework due to unambiguous similarities in the phenomenology accompanying the transition to the kinetically arrested state. However, the limits of this unifying scenario are emerging as the matter is further investigated: a deeper comprehension of the differences and the common fea-

tures of gels and glasses in colloids is necessary and lively debated in the up-to-date literature.

In Laponite suspensions -the system under investigation in the present work- nanometric size disks form a charged colloidal dispersion with a rich phase diagram. The competition between attractive and repulsive interactions and/or the anisotropy of the potential that originates the complexity of the phase diagram and the existence of several aggregation processes. Therefore, in recent years, Laponite suspensions have been widely studied not only for the important industrial applications [6] but especially for their peculiar experimental/theoretical properties [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. The first Dynamic Light Scattering (DLS) study [8] on this system has shown a slowing down of its dynamics (aging) as it evolves towards equilibrium. Therefore evolution with respect to waiting time from a liquid to a gel/glass state has been usually investigated for samples at clay concentration of $C_w = 3\%$ and at salt concentration of $C_s = 1 \times 10^{-4} M$. A recent complete DLS study in a wide range of clay and salt concentrations has permitted to individuate a surprising final arrested state not only for high but also for very low clay concentrations [13], at variance to previous [7] and recent [11] proposed phase diagrams. The aging time evolution from the initial liquid to the final arrested state occurs in a time that strongly depends on salt and clay concentrations and that increases as clay and/or salt concentrations are decreased [13], reaching the order of some months for $C_s = 1 \times 10^{-4} M$ and $C_w = 0.3\%$. The differences in the aging time evolution of both the raw spectra and the parameters obtained by their analysis have also permitted to distinguish between two different routes to reach two final non ergodic states at low and high clay concentrations [13](see Fig. 6 of [20]). The mechanisms that originate the existence of two different non ergodic states are a very interesting point. Moreover, whether or not these two states correspond to really different structures and what is the nature of these arrested states are up to now open and intriguing questions.

In this letter we give the first direct experimental evidence of the existence of two different arrested states in

Laponite suspensions and of their nature. The study of the aging time evolution of both the dynamic and the static structure factors has been performed through the combination of DLS and Small Angle X-rays Scattering (SAXS) techniques. These measurements permit to observe directly the evolution with aging time of the system and to distinguish between final inhomogeneous and homogeneous states resolving the longstanding controversy about the gel or glass nature of Laponite arrested state [10, 11]. More generally, while the signature for the time evolution of a gel was quite well known [21] this is the first experimental evidence of the $S(Q)$ time evolution for two different arrested states obtained only by changing sample's volume fraction.

Laponite suspensions were prepared in a glove box under N_2 flux and were always kept in safe atmosphere to avoid samples degradation [22]. The powder, manufactured by Laporte Ltd, was firstly dried in an oven at $T=400$ C for 4 hours and it was then dispersed in pure deionized water ($C_s \simeq 10^{-4}$ M), stirred vigorously for 30 minutes and filtered soon after through $0.45 \mu m$ pore size Millipore filters. The same identical protocol has been strictly followed for the preparation of each sample, fundamental condition to obtain reliable and reproducible results as also recently reported by [23]. The starting aging time ($t_w=0$) is defined as the time when the suspension is filtered. Samples were placed and sealed in thin glass capillaries with a diameter of 2 mm to be used both for DLS and SAXS measurements. As already discussed, the waiting time evolution of the aging dynamics requires few hours for high clay concentrations and months for low ones. Therefore only the aging of samples at high concentrations can be directly followed during allocated SAXS beamtime. To investigate samples at low concentrations, nominally identical concentration samples have been prepared at different dates starting three months before the planned experiment, so to have different waiting times at the moment of the measurements.

DLS experiments were carried out using an ALV goniometer fitted with a toluene bath. The incident laser wavelength was a diode pumped, frequency doubled Nd-YAG 30 mW laser ($\lambda = 532$ nm). The scattered intensity was recorded with an avalanche photodiode. The intensity correlation function was directly obtained as $g_2(Q, t) = \langle I(Q, t)I(Q, 0) \rangle / \langle I(Q, 0) \rangle^2$, where Q is the modulus of the scattering wave vector defined as $Q = (4\pi n/\lambda)\sin(\theta/2)$. In the present experiment $\theta=90^\circ$ and the acquisition time of each $g_2(Q, t)$ was 120 s.

SAXS measurements were performed at the High Brilliance beam line (ID2) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France using a 10 m pinhole SAXS instrument. The incident x-ray energy was fixed at 12.6 keV. The form factor $F(Q)$ was measured using a flow-through capillary cell. In SAXS data analysis the corrections for empty cell and water have been taken into account. The measured structure factor has been obtained as $S^M(Q) = I(Q)/F(Q)$. Figure 1 shows as an example the waiting time evolution of both the clay density

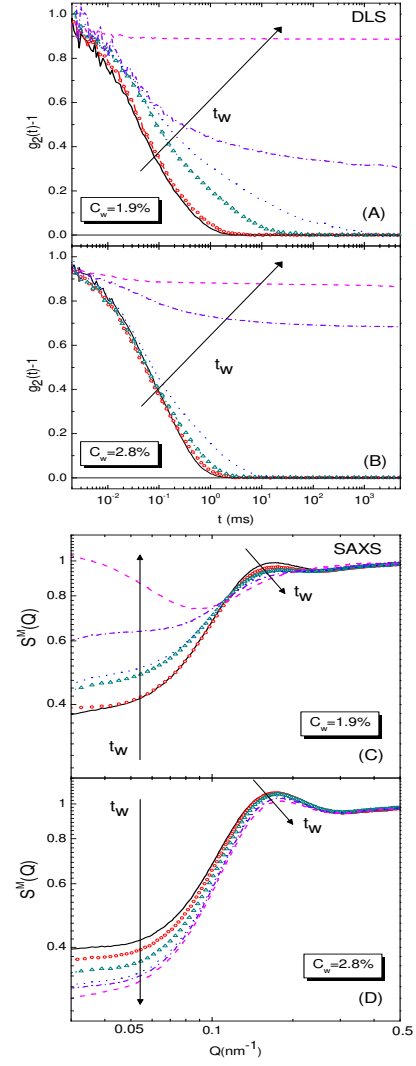


FIG. 1: (COLOR ONLINE) Evolution of the time autocorrelation functions (top panels) and of the measured structure factors (bottom panels) as a function of the waiting time t_w (same waiting times - same lines) for two different Laponite concentrations: a low one, $C_w = 1.9\%$ ((A) and (C) panels) and a high one, $C_w = 2.8\%$ ((B) and (D) panels).

auto-correlation functions (top panels) and the measured structure factors (low panels) for samples in the low and high concentration regions, at $C_w = 1.9\%$ ((A) and (C) panels) and $C_w = 2.8\%$ ((B) and (D) panels) respectively. The same sample was measured with the two techniques, DLS and SAXS (same lines in the top and bottom panels correspond to roughly same waiting time) and therefore a clear and direct comparison between the dynamic and static structure factor behaviors can be obtained. While, in fact, static light scattering measurements on Laponite samples have been previously carried out [8, 10, 15], the full evolutions of the structure factor with waiting times for both low and high concentration samples have never been reported.

From Fig. 1 the difference in the behavior of low and

high concentration samples is striking. For the high concentration sample ((B) and (D) panels of Fig. 1) there are no significant changes in the structure factor profiles while the sample crosses the ergodic/non ergodic transition (from dot to dashdot and dash curves). As the system is performing aging there is in fact only a progressive and slow decrease in the intensity at very low Q and a very small shift of the main peak to higher Q values. On the contrary, for the low concentration sample ((A) and (C) panels of Fig. 1) there is an evident change of the static structure factor as the sample ages and approaches the non ergodic state (from dot to dashdot and dash curves) specifically a progressive increased excess of scattering is observed at low Q values. Moreover, also a change in the shape of the curve and a shift of the main peak to higher Q values can be recognized. These differences are the clear evidence that the two samples are reaching the final non ergodic states following different routes [13] and, furthermore, that the two final arrested states are actually different.

The same behavior shown in panels A and C has been found for all the investigated low concentration samples. In Fig. 2 the static structure factors measured for three different low ($C_w < 2.0\%$) Laponite concentrations in correspondence of the full decay (small waiting time, lines) and incomplete decay (long waiting time, symbols) of the DLS spectra are shown. Due to different aging "velocity", we show here the $S^M(Q)$ at the same t_w/t_w^∞ , being t_w^∞ the C_w -dependent arrest time, as defined in Ref. [13]. It is clear that in the low Q region the same increase of intensity is found as the sample arrests. Moreover this excess of scattering at low Q increases as Laponite concentration is decreased. This indicates the existence of strong inhomogeneity in the suspension, that we attribute to the formation of a network which -as the aging time goes by- grows and eventually forms a gelled network. Also observable is the disappearance of the main peak and/or its shift to higher Q values. On the contrary, none of these features is observed for the high concentration ($C_w > 2.0\%$) samples where all the measurements have shown the same trend as the one drawn in panel (D) of Fig. 1. This indicates the homogeneity of the high C_w arrested state. The observed concentration dependence of the low Q scattering intensity seems to suggest that the transition between the two different final states is not discontinuous but the arrested state becomes more and more homogeneous increasing clay concentration. Summarizing, the data reported here give a clear proof of the existence of two structurally different arrested states in Laponite suspensions, completing the information -already reported in literature [13]- that low and high clay concentrations reaches the arrested state following two different routes. Static structure factor measurements, indeed, show an excess of scattering in the low Q region for the low concentration samples, thus indicating the formation of an inhomogeneous state, while for the high concentration samples the $S^M(Q)$ data are in agreement with the formation of a homogeneous arrested

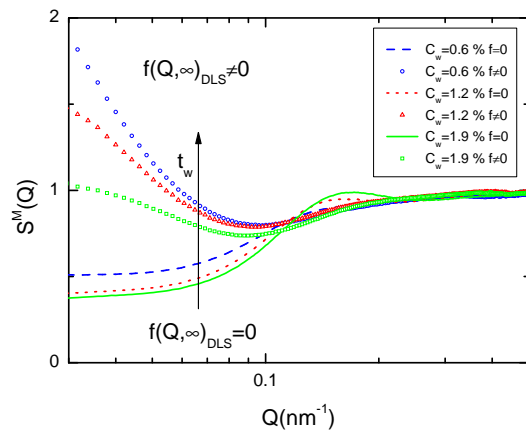


FIG. 2: (COLOR ONLINE) Waiting time evolution of the static structure factors from full decay ($f(Q, \infty) = 0$) to incomplete decay ($f(Q, \infty) \neq 0$) in the corresponding DLS spectra for three different low Laponite concentrations at $t_w \approx 1.2 t_w^\infty$.

state.

The present experimental findings, together with the phenomenology associated to gel and glass formation in colloids allow to speculate on the nature of the observed arrested states. Despite the apparent simple definition that "colloidal gels are arrested state of matter at low density where the particles are tightly bonded to each other so that the thermo-reversible bonds is comparable or longer than the experimental observation time", the essence of the (colloidal) gel state is still under debate [24]. In this context, it is important to stress that sometimes the discussion on what is a gel and a glass becomes a nominalistic dispute. In fact, the formation of a bonding gel, which in a part of the colloidal community provides indication of gel formation, for another part of the scientific community, would be rather classified as glass formation [24]. In this sense we can follow the proposition that in a "gel" the attraction between colloidal particles is the leading mechanism for gelation, while a "glassy state" can be driven either by repulsion (hard-sphere or Wigner glass) or by attraction (attractive glass). Moreover, while the gel state is characterized by structural inhomogeneities (signalled by a non-trivial low- Q signal in the scattering intensity) the glass is structurally homogeneous [1].

On the ground of the previous discussion the low clay concentration inhomogeneous arrested state can be considered as a gel while the high concentrated homogeneous as a glass. Moreover, in Laponite, increasing salt concentrations the arrested states are still observed and occur even more rapidly [10, 13]. This observation is in clear contradiction with the formation of a colloidal glass induced by strong repulsive interactions that are decreased (due to effect of screening) as the ionic strength is increased. Therefore, the attractive interaction must be responsible of the final arrested state. For these reasons

we can call the homogeneous state at high clay concentrations an attractive glass, i.e. a homogeneous state governed by attractive interactions (that can also be called homogeneous gel). On the contrary, in the low concentration region, the inhomogeneous state is compatible with the formation of a gel state where the aging dynamics is supposed to be characterized by the growth of region of strongly correlated platelets which increases in size and, eventually, span all over the systems at the gel transition.

It is worth to note that the features of this concentration region fit with those of the newly discovered *equilibrium bonding gel* region [1], a state found in low density colloids with anisotropic interactions. In fact, the interaction potential between Laponite platelets is certainly non spherical, with privileged relative orientation, an aspect that probably has not been properly accounted for in previous studies. Moreover, the waiting time evolution of $S(Q)$ in Fig. 1C strongly resembles the temperature evolution of $S(Q)$ of Fig.5 (a) of Ref.[5] obtained in simulation of a valence-limited colloidal system. The increased intensity at small wave vectors of $S(Q)$ as waiting time (temperature) is increased (decreased) indicates that the system becomes more and more compressible, with large inhomogeneities that can be seen as an echo of the nearby phase separation or, equivalently, as a consequence of building up a fully connected network. In fact one can suppose that as the time goes by the system feels more and more the attraction approaching, through successive equilibrium states, the final arrested state as the ideal systems [5] do decreasing temperature. Also the evolution of the $S(Q)$ with concentration seems to be in qual-

itative agreement with Fig.5(b) of Ref.[5]: moving away from the spinodal line (increasing C_w) the $Q \rightarrow 0$ peak decreases and the nearest neighbor peak grows, signaling the increasing importance of the packing. It is important to underline that, besides the qualitative agreement between the behavior of the model and Laponite suspensions no quantitative comparison can be done between the systems due to Laponite peculiarity. Therefore, at present, we are not also able to locate the spinodal line in Laponite suspensions. It could be in fact possible that some of the samples at very low concentrations are "inside" the spinodal line and that for those systems a separation phase at very long waiting times could take place.

In conclusion, the results reported here, resolve the longstanding controversy about the final arrested state in Laponite suspensions [10, 11]: both an inhomogeneous and a homogeneous state exist. They are reached -as the system ages- following two different dynamic routes [13]. The existence of two different arrested states in this charged colloidal system with a non spherical potential (further complicated by the presence of charges), depending only on its concentration, gives a proof of the strong connection existing between the "gel" and "glass" states. A common experimental and theoretical effort for the understanding of the still puzzling liquid-gel/glass transition and a theoretical investigation about the features of the different arrested states in presence of charged non spherical potentials, are needed.

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